CELLULOSE SUPPORTED TRANSITION METAL (Cu, Pd) CATALYSTS FOR CARBON-CARBON AND CARBON-NITROGEN BONDS FORMATION REACTIONS

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

°C	degree centigrade
g	gram
cm^{-1}	per centimetre
δ	chemical shift
equiv	equivalence
Hz	hertz
h	hour
L	litre
MHz	mega hertz
μm	micrometre
mg	milligram
ml	millilitre
mmol	millimole
mol	mole
mol L^{-1}	mole per litre
nm	nanometre
%	percentage
M	molar
N	normality
sec	second
cm^2	square of centimetre
mol%	mole percentage

LIST OF ABBREVIATIONS

α	alpha
Ar	aromatic
β	beta
^{13}C NMR	carbon nuclear magnetic resonance
J	coupling constant
d	doublet
dd	doublet of doublet
EDX	energy dispersive X-ray spectroscopy
FTIR	fourier transform infrared spectroscopy
HR-TEM	high resolution transmission electron microscopy
HR-SEM	high resolution scanning electron microscopy
H-bond	hydrogen bond
IR	infrared
ICP-AES	inductively coupled plasma atomic emission spectroscopy
m	multiplet
^{1}H NMR	proton nuclear magnetic resonance
pH	potential of hydrogen
q	quartet
s	singlet
TLC	thin layer chromatography
t	triplet
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

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ABSTRAK

Kajian ini terutama berkaitan dengan sintesis, pencirian, dan aplikasi mangkin logam heterogen berasaskan selulosa berfungsi untuk pelbagai jenis tindak balas penggandingan silang. Tindak balas penggandingan silang secara amnya dijalankan dengan kehadiran kompleks logam homogen. Cabaran eksperimen untuk melakukan tindak balas katalitik homogen adalah rumit disebabkan kesukaran pemisahan produk daripada campuran tindak balas, serta ketidakupayaan untuk menggunakan semula mangkin logam. Untuk mengatasi masalah ini, penyelidik-penyelidik telah mengkaji penggunaan pelbagai sokongan pepejal heterogen untuk spesies pemangkin logam seperti nanotiub karbon, grafin, silikat, polimer, oksida logam, dan pelbagai bahan bukan organik hibrid. Walaupun banyak protokol yang berekonomi dan mampan telah digunakan oleh para penyelidik yang berdedikasi dalam pengkajian tindak balas penggandingan silang yang mesra alam, tetapi masih terdapat permintaan yang tinggi untuk meneroka pemangkin yang lebih berkesan untuk tindak balas transformasi kimia. Pada masa kini, sains dan teknologi beralih ke arah persekitaran yang mesra alam, dan proses untuk mengkaji pengeluaran bahan kimia halus. Dalam perspektif ini, biopolimer semulajadi (selulosa) boleh dipertimbangkan sebagai bahan sokongan padu yang boleh diterima kerana kelebihannya seperti mudah diperolehi, mempunyai ketumpatan yang rendah, boleh diperbaharui, ketersediaan, kos rendah dan sifat kimia dan mekanikal yang menarik. Oleh itu, selulosa semulajadi akan menjadi sokongan padat sempurna sebagai mangkin. Dalam kajian ini, selulosa tongkol buah jagung telah diasingkan dan tulang belakang selulosa diubahsuai secara kimia melalui pempolimeran. Kumpulan polimer berfungsi yang dihasilkan telah ditukar menjadi ligand pengkelat poli(amidoksim) yang sesuai. Selulosa poli(amidoksim) mudah menjalani tindak balas kompleks dengan rawatan garam logam (Pd/Cu) untuk menghasilkan logam poli(amidoksim) heterogen yang berasakan selulosa. Kompleks palladium yang berasaskan selulosa mempamerkan aktiviti pemangkin tinggi (0.1 hingga 0.05 mol%) terhadap tindak balas penggandingan silang Mizoroki-Heck aril halida dengan pelbagai olefin untuk memberikan produk gandingan sehingga hasil 97%. Pengeluaran elektron aril halida dapat memproses hasil yang lebih tinggi berbanding dengan aril halida yang menderma elektron. Kompleks palladium juga digunakan untuk sintesis Ozagrel, perencat thromboxane A_2-sintetas melalui tindak balas Mizoroki-Heck dengan penghasilan 88%. Kompleks tembaga (amidoksim) yang berasaskan selulosa digunakan untuk tindak balas Clik [Cu (II) 1 hingga 0.05 mol%] daripada azida organik dengan alkil terminal untuk membekalkan triazol sehingga hasil 96%. Selain itu, nanopartikel tembaga telah disediakan dari kompleks tembaga dan distabilkan dangan baiknya oleh ligan poli(amidoksim). Nanopartikel tembaga tersebut mempercepatkan tindak balas amina alifatik chemoselective Aza-Michael [Cu(0), 0.1 hingga 0.005 mol%] dengan α, β-sebatian-sebatian yang tidak tepu dengan cekap untuk memberikan penghasilan sehingga 95%. Tambahan pula, semua pemangkin polimer berasaskan selulosa adalah mudah diperolehi semula darpada campuran tindak balas dan digunakan beberapa kali tanpa kehilangan aktiviti permangkin yang ketara.

ABSTRACT

This research mainly deals with the synthesis, characterization, and applications of functionalized cellulose supported heterogeneous metal catalysts for various types of cross-coupling reactions. Cross-coupling reactions generally proceed in the presence of homogeneous metal complexes. The practical limits to perform homogeneous catalysis reactions are complicated due to the difficulty in the separation of the product from the reaction mixture, as well as the inability to reuse the metal catalysts. To overcome these problems, scientific communities have investigated the use of various heterogeneous solid supports for metal catalyst species such as carbon nanotubes, graphene, silicates, polymers, metal oxides, and various hybrid inorganic materials. Although many economic and sustainable protocols have been employed by researchers dedicated to the development of green processes for cross-coupling reactions, there is still a high demand to explore more efficient catalysts for chemical transformation reactions. Nowadays, science and technology are shifting towards environmentally friendly, sustainable resources, and processes to investigate low-cost production of fine chemicals. In this perspective, natural biopolymers (cellulose) could be considered as acceptable solid support materials because of their promising merits such as being largely abundant in nature, having low density, bio-renewability, universal availability, low-cost and interesting chemical and mechanical properties. Therefore, natural cellulose would be a perfect solid support for catalysts. In this study, corn-cob cellulose was isolated from bio-waste corn-cobs, and the backbone of the cellulose was chemically modified through polymerization. The resulting polymeric functional group was converted into suitable poly(amidoxime) chelating ligand. The cellulose-supported poly(amidoxime) readily underwent a complexation reaction by treatment with metal (Pd/Cu) salts to give the corresponding cellulose-supported heterogeneous poly(amidoxime) metal complexes. The cellulose-supported palladium complex exhibited a high catalytic activity (0.1 to 0.05 mol%) towards Mizoroki-Heck cross-coupling reactions of aryl halides with a variety of olefins to give the corresponding coupling products of up to 97% yield. The electron withdrawing aryl halides processes higher yields compare to electron donating aryl halides. The palladium complex was also applied to the synthesis of Ozagrel, a thromboxane A_2-synthetase inhibitor through Mizoroki-Heck reaction with 88% yield. The cellulose-supported poly(amidoxime) copper complex was applied to the Click reaction [Cu(II) 1 to 0.05 mol%] of organic azide with terminal alkyne to afford triazole in up to 96% yield. Moreover, copper nanoparticles were prepared from the copper complex and well stabilized by the poly(amidoxime) ligands. The copper nanoparticles were efficiently promoted the chemoselective Aza-Michael reaction [Cu(0) 0.1 to 0.005 mol%] of aliphatic amines with α,β-unsaturated compounds to give addition products in up to 95% yield. Additionally, all polymeric cellulose supported catalysts were easy to recover from the reaction mixture and reused several times without significant loss of their catalytic activities.

REFERENCES

Aiken, J. D., & Finke, R. G. (1999). A review of modern transition-metal nanoclusters: their synthesis, characterization, and applications in catalysis. *Journal of Molecular Catalysis A: Chemical*, *145*(1-2), 1–44.

Amara, Z., Caron, J., & Joseph, D. (2013). Recent contributions from the asymmetric Aza-Michael reaction to alkaloids total synthesis. *Natural Product Reports*, *30*(9), 1211–1225.

Amatore, C., & Jutand, A. (2000). Anionic Pd(0) and Pd(II) Intermediates in Palladium-Catalyzed Heck and Cross-Coupling Reactions, *Accounts of Chemical Research*, *33*(5), 314–321.

Anan, N. A., Hassan, S. M., Saad, E. M., Butler, I. S., & Mostafa, S. I. (2011). Preparation, characterization and pH-metric measurements of 4-hydroxysalicylidenechitosan Schiff-base complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ru(III), Rh(III), Pd(II) and Au(III). *Carbohydrate Research*, *346*(6), 775–793.

Anastas, P., & Eghbali, N. (2010). Green Chemistry: Principles and Practice. *Chemical Society Reviews*, *39*(1), 301–312.

Anastas, P. T., & Kirchhoff, M. M. (2002). Origins, current status, and future challenges of green chemistry. *Accounts of Chemical Research*, *35*(9), 686–694.

Andrus, M. B., Song, C., & Zhang, J. (2002). Palladium−Imidazolium Carbene Catalyzed Mizoroki−Heck Coupling with Aryl Diazonium Ions. *Organic Letters*, *4*(12), 2079–2082.

Anil Kumar, B. S. P., Harsha Vardhan Reddy, K., Karnakar, K., Satish, G., & Nageswar, Y. V. D. (2015). Copper on chitosan: An efficient and easily recoverable heterogeneous catalyst for one pot synthesis of 1,2,3-triazoles from aryl boronic acids in water at room temperature. *Tetrahedron Letters*, *56*(15), 1968–1972.

Appukkuttan, P., Dehaen, W., Fokin, V. V, & Eycken, E. Van Der. (2004). A Microwave-Assisted Click Chemistry Synthesis of 1 , 4-Disubstituted 1, 2, 3 Triazoles via a copper(I)-Catalyzed Three-Component Reaction. *Organic Letters*, *6*(23), 4223–4225.

Aragão-Leoneti, V., Campo, V. L., Gomes, A. S., Field, R. A., & Carvalho, I. (2010). Application of copper(I)-catalysed azide/alkyne cycloaddition (CuAAC) "Click chemistry" in carbohydrate drug and neoglycopolymer synthesis. *Tetrahedron*, *66*(49), 9475–9492.

Azizi, N., Baghi, R., Ghafuri, H., Bolourtchian, M., & Hashemi, M. (2010). Silicon tetrachloride catalyzed Aza-Michael addition of amines to conjugated alkenes under solvent-free conditions. *Synlett*, (3), 379–382.

Bagherzadeh, M., Ashouri, F., Hashemi, L., & Morsali, A. (2014). Supported Pd nanoparticles on Mn-based metal-organic coordination polymer: Efficient and recyclable heterogeneous catalyst for Mizoroki-Heck cross coupling reaction of terminal alkenes. *Inorganic Chemistry Communications*, *44*, 10–14.

Bakherad, M., Keivanloo, A., Bahramian, B., & Jajarmi, S. (2013). Suzuki, Heck, and copper-free Sonogashira reactions catalyzed by 4-amino-5-methyl-3-thio-1,2,4-triazole-functionalized polystyrene resin-supported Pd(II) under aerobic conditions in water. *Journal of Organometallic Chemistry*, *724*, 206–212.

Bakherad, M., Keivanloo, A., & Samangooei, S. (2012). Solvent-free Heck and copper-free Sonogashira cross-coupling reactions catalyzed by a polystyrene-anchored Pd(II) phenyldithiocarbazate complex. *Tetrahedron Letters*, *53*(43), 5773–5776.

Bakherad, M., Keivanloo, A., & Samangooei, S. (2014). Poly(vinyl chloride)-supported Pd(II) complex as an efficient catalyst for Heck and Cu-free Sonogashira reactions under aerobic conditions. *Chinese Journal of Catalysis*, *35*, 324-328.

Barot, N., Patel, S. B., & Kaur, H. (2016). Nitro resin supported copper nanoparticles: An effective heterogeneous catalyst for C-N cross coupling and oxidative C-C homocoupling. *Journal of Molecular Catalysis A: Chemical*, *423*, 77–84.

Baruah, D., Das, R. N., Hazarika, S., & Konwar, D. (2015). Biogenic synthesis of cellulose supported Pd(0) nanoparticles using hearth wood extract of Artocarpus lakoocha Roxb-A green, efficient and versatile catalyst for Suzuki and Heck coupling in water under microwave heating. *Catalysis Communications*, *72*, 73–80.

Bauer, J. E., Occelli, M. L., Williams, P. M., & McCaslin, P. C. (1993). Heterogeneous catalyst structure and function: review and implications for the analysis of dissolved organic carbon and nitrogen in natural waters. *Marine Chemistry*, *41*(1-3), 75–89.

Beletskaya, I. P., & Kustov, L. M. (2010). Catalysis as an important tool of green chemistry. *Russian Chemical Reviews*, *79*(6), 441–461.

Bo, K. L., Wu, Q., Xue, Q. Q., De, S. L., & Xian, F. L. (2007). *N*-Methylimidazole as a promising catalyst for the Aza-Michael addition reaction of *N*-heterocycles. *Synthesis*, (17), 2653–2659.

Bolton, A. J. (1994). Natural Fibers for Plastic Reinforcement. *Materials Technology*, *9*(1-2), 12–20.

Brown, R. M. (2004). Cellulose Structure and Biosynthesis: What is in Store for the 21st Century? *Journal of Polymer Science, Part A: Polymer Chemistry*, *42*(3), 487–495.

Casares, J. A., Espinet, P., Fuentes, B., & Salas, G. (2007). Insights into the mechanism of the Negishi reaction: ZnRX versus ZnR_2 reagents. *Journal of the American Chemical Society*, *129*(12), 3508–3509.

Chao-Jun, L., & Anastas, P. (2012). Green Chemistry: present and future. *Chemical Society Reviews*, (41), 1413–1414.

Chaudhuri, M. K., Hussain, S., Kantam, M. L., & Neelima, B. (2005). Boric acid: A novel and safe catalyst for Aza-Michael reactions in water. *Tetrahedron Letters*, *46*(48), 8329–8331.

Chavan, P. V, Pandit, K. S., Desai, U. V, Kulkarni, M. A, & Wadgaonkar, P. P. (2014). Cellulose supported cuprous iodide nanoparticles (Cell-CuI NPs): a new heterogeneous and recyclable catalyst for the one pot synthesis of 1,4-disubstituted -1,2,3-triazoles in water. *RSC Advances*, *4*(79), 42137–42146.

Cole-Hamilton, D. J. (2003). Homogeneous Catalysis-New Approaches to Catalyst Separation, Recovery, and Recycling. *Science*, *299*(5613), 1702–1706.

Cordovilla, C., Bartolomé, C., Martínez-Ilarduya, J. M., & Espinet, P. (2015). The stille reaction, 38 years later. *ACS Catalysis*, *5*(5), 3040–3053.

Corma, A, Garcia, H., & Llabres, I. X. F. X. (2010). Engineering metal organic frameworks for heterogeneous catalysis. *Chemical Reviews*, *110*(8), 4606–4655.

Dahou, W., Ghemati, D., Oudia, A., & Aliouche, D. (2010). Preparation and biological characterization of cellulose graft copolymers. *Biochemical Engineering Journal*, *48*, 187–194.

Dai, L., Zhang, Y., Dou, Q., Wang, X., & Chen, Y. (2013). Chemo/regioselective Aza-Michael additions of amines to conjugate alkenes catalyzed by polystyrene-supported $AlCl_3$. *Tetrahedron*, *69*(6), 1712–1716.

Dai, Q., Gao, W., Liu, D., Kapes, L. M., & Zhang, X. (2006). Triazole-based monophosphine ligands for palladium-catalyzed cross-coupling reactions of aryl chlorides. *The Journal of Organic Chemistry*, *71*, 3928–3934.

Das, B., & Chowdhury, N. (2007). Amberlyst-15: An efficient reusable heterogeneous catalyst for Aza-Michael reactions under solvent-free conditions. *Journal of Molecular Catalysis A: Chemical*, *263*(1-2), 212–215.

Datta, A., Adhikary, J., Chatterjee, S., Ghosh, D., Khamarui, S., & Chattopadhyay, T. (2016). Synthesis and characterization of a magnetically separable novel Fe_3O_4 @L-DOPA@Cu(II) nanocatalyst (L-DOPA = L-3,4-dihydroxyphenyylalanine): Asymmetric Aza-Michael addition reaction. *Inorganica Chimica Acta*, *444*, 209–216.

Dhepe, P. L., & Fukuoka, A. (2007). Cracking of cellulose over supported metal catalysts. *Catalysis Surveys from Asia*, *11*(4), 186–191.

Di Lena, F., & Matyjaszewski, K. (2010). Transition metal catalysts for controlled radical polymerization. *Progress in Polymer Science*, *35*(8), 959–1021.

Dijkstra, H. P., Van Klink, G. P. M., & Van Koten, G. (2002). The use of ultra-and nanofiltration techniques in homogeneous catalyst recycling. *Accounts of Chemical Research*, *35*(9), 798–810.

Du, Q., Zhang, W., Ma, H., Zheng, J., Zhou, B., & Li, Y. (2012). Immobilized palladium on surface-modified Fe_3O_4/SiO_2 nanoparticles: As a magnetically separable and stable recyclable high-performance catalyst for Suzuki and Heck cross-coupling reactions. *Tetrahedron*, *68*(18), 3577–3584.

Dunn, P. J. (2012). The importance of Green Chemistry in Process Research and Development. *Chemical Society Reviews*, *41*(4), 1452–1461.

Echeandia, S., Pawelec, B., Barrio, V. L., Arias, P. L., Cambra, J. F., Loricera, C. V., & Fierro, J. L. G. (2014). Enhancement of phenol hydrodeoxygenation over Pd catalysts supported on mixed HY zeolite and Al_2O_3. An approach to O-removal from bio-oils. *Fuel*, *117*, 1061–1073.

Ehrentraut, A, Zapf, A, & Beller, M. (2000). A New Efficient Palladium Catalyst for Heck Reactions of Deactivated Aryl Chlorides. *Synlett : Accounts and Rapid Communications in Synthetic Organic Chemistry*, (11), 1589–1592.

Elazab, H. A., Siamaki, A. R., Moussa, S., Gupton, B. F., & El-Shall, M. S. (2015). Highly efficient and magnetically recyclable graphene-supported Pd/Fe_3O_4 nanoparticle catalysts for Suzuki and Heck cross-coupling reactions. *Applied Catalysis A: General*, *491*, 58–69.

Espinet, P., & Echavarren, A. M. (2004). The mechanisms of the Stille reaction. *Angewandte Chemie International Edition*, *43*(36), 4704–4734.

Favier, I., Madec, D., Teuma, E., & Gomez, M. (2011). Palladium Nanoparticles Applied in Organic Synthesis as Catalytic Precursors. *Current Organic Chemistry*, *15*(18), 3127–3174.

Felpin, F. X., Fouquet, E., & Zakri, C. (2008). Heck cross-coupling of aryldiazonium tetrafluoroborate with acrylates catalyzed by palladium on charcoal. *Advanced Synthesis and Catalysis*, *350*(16), 2559–2565.

Fernández-García, L., Blanco, M., Blanco, C., Álvarez, P., Granda, M., Santamaría, R., & Menéndez, R. (2016). Graphene anchored palladium complex as efficient and recyclable catalyst in the Heck cross-coupling reaction. *Journal of Molecular Catalysis A: Chemical*, *416*, 140–146.

Fu, G. T., Wu, R., Liu, C., Lin, J., Sun, D. M., & Tang, Y. W. (2015). Arginine-assisted synthesis of palladium nanochain networks and their enhanced electrocatalytic activity for borohydride oxidation. *RSC Advances*, *5*(23), 18111–18115.

Fustero, S., Pina, B., Salavert, E., Navarro, A., Ramírez de Arellano, M. C., & Fuentes, A. S. (2002). New strategy for the stereoselective synthesis of fluorinated beta-amino acids. *The Journal of Organic Chemistry*, *67*(14), 4667–4679.

García, A., Gandini, A., Labidi, J., Belgacem, N., & Bras, J. (2016). Industrial and crop wastes: A new source for nanocellulose biorefinery. *Industrial Crops and Products*, *93*, 26–38.

Gholinejad, M., & Jeddi, N. (2014). Copper nanoparticles supported on agarose as a bioorganic and degradable polymer for multicomponent Click synthesis of 1,2,3-triazoles under low copper loading in water. *ACS Sustainable Chemistry and Engineering*, *2*(12), 2658–2665.

Girard, S. A., Knauber, T., & Li, C. J. (2014). The cross-dehydrogenative coupling of C_{sp3} -H bonds: A versatile strategy for C-C bond formations. *Angewandte Chemie International Edition*, *53*(1), 74–100.

Gladysz, J. A. (2001). Recoverable catalysts. Ultimate goals, criteria of evaluation, and the green chemistry interface. *Pure and Applied Chemistry*, *73*(8), 1319–1324.

Gøgsig, T. M., Nielsen, D. U., Lindhardt, A. T., & Skrydstrup, T. (2012). Palladium catalyzed carbonylative Heck reaction affording monoprotected 1,3-ketoaldehydes. *Organic Letters*, *14*(10), 2536–2539.

Gong, H. P., Quan, Z. J., & Wang, X. C. (2016). Palladium catalyzed Mizoroki–Heck reaction of pyrimidin-2-yl tosylates with aromatic and aliphatic olefins. *Tetrahedron*, *72*(16), 2018–2025.

Guibal, E. (2005). Heterogeneous catalysis on chitosan-based materials: A review. *Progress in Polymer Science (Oxford)*, *30*(1), 71–109.

Haas, D., Hammann, J. M., Greiner, R., & Knochel, P. (2016). Recent Developments in Negishi Cross-Coupling Reactions. *ACS Catalysis*, *6*(3), 1540–1552.

Hajipour, A. R., Tadayoni, N. S., & Khorsandi, Z. (2016). Magnetic iron oxide nanoparticles-N-heterocyclic carbene-palladium(II): a new, efficient and robust recyclable catalyst for Mizoroki-Heck and Suzuki-Miyaura coupling reactions. *Applied Organometallic Chemistry*, *30*(7), 590–595.

Haron, M. J., Tiansih, M., Ibrahim, N. A., Kassim, A., & Wan Yunus, W. M. Z. (2009). Sorption of Cu(II) by poly(hydroxamic acid) chelating exchanger prepared from pol(ymethyl acrylate) grafted oil palm empty fruit bunch (OPEFB). *BioResources*, *4*(4), 1305–1318.

Hartmann, M., & Kevan, L. (1999). Transition-Metal Ions in Aluminophosphate and Silicoaluminophosphate Molecular Sieves: Location, Interaction with Adsorbates and Catalytic Properties. *Chemical Reviews*, *99*(3), 635–664.

Hattori, H. (2001). Solid base catalysts: Generation of basic sites and application to organic synthesis. *Applied Catalysis A: General*, *222*(1-2), 247–259.

Heck, R. F. (1979). Palladium-catalyzed reactions of organic halides with olefins. *Accounts of Chemical Research*, *12*(1968), 146-151.

Heck, R. F., & Nolley, J. P. (1972). Palladium-catalyzed vinylic hydrogen substitution reactions with aryl, benzyl, and styryl halides. *The Journal of Organic Chemistry*, *37*(14), 2320–2322.

Himaja, M., Poppy, D., & Asif, K. (2011). Green Technique-Solvent Free Synthesis and Its Advantages. *International Journal of Research in Ayurveda & Pharmacy*, *2*(24), 1079–1086.

Himo, F., Lovell, T., Hilgraf, R., Rostovtsev, V. V., Noodleman, L., Sharpless, K. B., & Fokin, V. V. (2005). Copper(I)-catalyzed synthesis of azoles. DFT study predicts unprecedented reactivity and intermediates. *Journal of the American Chemical Society*, *127*(1), 210–216.

Hope, G. A., Woods, R., Parker, G. K., Buckley, A. N., & McLean, J. (2010). A vibrational spectroscopy and XPS investigation of the interaction of hydroxamate reagents on copper oxide minerals. *Minerals Engineering*, *23*(11-13), 952–959.

Hosseini, S. G., & Abazari, R. (2015). A facile one-step route for production of CuO, NiO, and CuO–NiO nanoparticles and comparison of their catalytic activity for ammonium perchlorate decomposition. *RSC Advances*, *5*(117), 96777–96784.

Huang, K., Xue, L., Hu, Y. C., Huang, M. Y., & Jiang, Y. Y. (2002). Catalytic behaviors of silica-supported starch-polysulfosiloxane-Pt complexes in asymmetric hydrogenation of 4-methyl-2-pentanone. *Reactive and Functional Polymers*, *50*(3), 199–203.

Huang, Z., Li, F., Chen, B., Xue, F., Chen, G., & Yuan, G. (2011). Nitrogen-rich copolymeric microsheets supporting copper nanoparticles for catalyzing arylation of N-heterocycles. *Applied Catalysis A: General*, *403*(1-2), 104–111.

Huisgen, R. (1963). 1,3-Dipolar Cycloadditions. Past and Future. *Angewandte Chemie International Edition*, *2*(10), 565–598.

Iranpoor, N., Firouzabadi, H., Motevalli, S., & Talebi, M. (2012). Palladium nanoparticles supported on silicadiphenyl phosphinite (SDPP) as efficient catalyst for Mizoroki-Heck and Suzuki-Miyaura coupling reactions. *Journal of Organometallic Chemistry*, *708-709*, 118–124.

Jadhav, S., Jagdale, A., Kamble, S., Kumbhar, A., & Salunkhe, R. (2016). Palladium nanoparticles supported on a titanium dioxide cellulose composite (PdNPs@TiO_2 – Cell) for ligand-free carbon–carbon cross coupling reactions. *RSC Advances*, *6*(5), 3406–3420.

Janssen, M., Müller, C., & Vogt, D. (2011). Recent advances in the recycling of homogeneous catalysts using membrane separation. *Green Chemistry*, *13*(9), 2247-2257.

Jun, C. (2004). Transition metal-catalyzed carbon–carbon bond activation.*Chemical Society Reviews, 33,* 610–618.

Kalidindi, S. B., & Jagirdar, B. R. (2012). Nanocatalysis and prospects of green chemistry. *ChemSusChem*, *5*(1), 65–75.

Kang, S., Choi, S., Ryu, H., & Yamaguchi T. (1998). Palladium-Catalyzed Coupling of Organolead Compounds with Olefins. *Journal of Organic Chemistry*, *63*(8), 5748–5749.

Karthikeyan, P., Muskawar, P. N., Aswar, S. A., Bhagat, P. R., & Sythana, S. K. (2012). Development of an efficient solvent free one-pot Heck reaction catalyzed by novel palladium(II) complex-via green approach. *Journal of Molecular Catalysis A: Chemical*,*358*, 112–120.

Keipour, H., Khalilzadeh, M. A., Hosseini, A., Pilevar, A., & Zareyee, D. (2012). An active and selective heterogeneous catalytic system for Michael addition. *Chinese Chemical Letters*, *23*(5), 537–540.

Khalafi-Nezhad, A., & Panahi, F. (2014). Size-Controlled Synthesis of Palladium Nanoparticles on a Silica–Cyclodextrin Substrate: A Novel Palladium Catalyst System for the Heck Reaction in Water. *ACS Sustainable Chemistry & Engineering*, *2*(5), 1177–1186.

Khazaei, A., Khazaei, M., & Rahmati, S. (2015). A green method for the synthesis of gelatin/pectin stabilized palladium nano-particles as efficient heterogeneous catalyst for solvent-free Mizoroki-Heck reaction. *Journal of Molecular Catalysis A: Chemical*, *398*, 241–247.

Khazaei, A., Rahmati, S., Hekmatian, Z., & Saeednia, S. (2013). A green approach for the synthesis of palladium nanoparticles supported on pectin: Application as a catalyst for solvent-free Mizoroki-Heck reaction. *Journal of Molecular Catalysis A: Chemical*, *372*, 160–166.

Kobayashi, S., Kakumoto, K., & Sugiura, M. (2002). Transition Metal Salts-Catalyzed Aza-Michael Reactions of Enones with Carbamates. *Organic Letters*, *4*(8), 1319–1322.

Koga, H., Azetsu, A., Tokunaga, E., Saito, T., Isogai, A., & Kitaoka, T. (2012). Topological loading of Cu(I) catalysts onto crystalline cellulose nanofibrils for the Huisgen Click reaction. *Journal of Materials Chemistry*, *22*(12), 5538-5542.

Kolb, H. C., & Sharpless, K. B. (2003). The growing impact of Click chemistry on drug discovery.*Drug Discovery Today*, *8*(24), 1128–1137.

Lasch, R., Fehler, S. K., & Heinrich, M. R. (2016). Hydrogen Peroxide Promoted Mizoroki-Heck Reactions of Phenyldiazenes with Acrylates, Acrylamides, and Styrenes. *Organic Letters*, *18*(7), 1586–1589.

Leclerc, J. P., & Fagnou, K. (2006). Palladium-Catalyzed Cross-Coupling Reactions of Diazine *N*-Oxides with Aryl Chlorides, Bromides, and Iodides. *Angewandte Chemie International Edition*, *45*(46), 7781–7786.

Lee, D., Taher, A., Hossain, S., & Jin, M. (2011). An Efficient and General Method for the Heck and Buchwald À Hartwig Coupling Reactions of Aryl Chlorides. *Organic Letters*, *13*(7), 5540–5543.

Lee, J., Farha, O. K., Roberts, J., Scheidt, K. A., Nguyen, S. T., & Hupp, J. T. (2009). Metal-organic framework materials as catalysts. *Chemical Society Reviews*, *38*(5), 1450–1459.

Liu, C. F., Ren, J. L., Xu, F., Liu, J. J., Sun, J. X., & Sun, R. C. (2006). Isolation and characterization of cellulose obtained from ultrasonic irradiated sugarcane bagasse. *Journal of Agricultural and Food Chemistry*, *54*(16), 5742–5748.

Liu, C., Zhang, H., Shi, W., & Lei, A. (2011). Bond formations between two nucleophiles: Transition metal catalyzed oxidative cross-coupling reactions. *Chemical Reviews*, *111*(3), 1780–1824.

Löber, S., Rodriguez-Loaiza, P., & Gmeiner, P. (2003). Supporting Information Available Click Linker : Efficient and High Yielding Synthesis of a New Family of SPOS Resins by 1 , 3-Dipolar Cycloaddition Experimental details : *Organic Letters*, *5*(10), 1753–1755.

Loo, M. H., Egan, D., Vaughan, E. D., Marion, D., Felsen, D., & Weisman, S. (1987). The Effect of the Thromboxane A2 Synthesis Inhibitor Oky-046 on Renal Function in Rabbits Following Release of Unilateral Ureteral Obstruction. *The Journal of Urology*, *137*(3), 571–576.

Lutfor, M. R., Sidik, S., Wan Yunus, W. M. Z., Ab Rahman, M. Z., Mansoor, A., & Jelas, H. (2001). Preparation and swelling of polymeric absorbent containing hydroxamic acid group from polymer grafted sago starch. *Carbohydrate Polymers*, *45*(1), 95–100.

Lutfor, M. R., Sidik, S., Yunus, W. M. Z. W. A. N., Rahman, M. Z. A., Mansor, A., & Haron, M. J. (2001). Synthesis and Characterization of Poly(hydroxamic acid) Chelating Resin from Poly(methyl acrylate)-Grafted Sago Starch. *Journal of Applied Polymer Science*, *79*, 1256–1264.

Lv, X., Wang, Z., & Bao, W. (2006). CuI catalyzed C-N bond forming reactions between aryl/heteroaryl bromides and imidazoles in [Bmim]BF_4. *Tetrahedron*, *62*(20), 4756–4761.

Mahdavi, H., & Sahraei, R. (2016). Synthesis and Application of Hyperbranched Polyester-Grafted Polyethylene (HBPE-g-PE) Containing Palladium Nanoparticles as Efficient Nanocatalyst. *Catalysis Letters*, *146*(5), 977–990.

Maluenda, I., & Navarro, O. (2015). Recent developments in the Suzuki-Miyaura reaction: 2010-2014. *Molecules*, *20*(5), 7528–7557.

Mandal , B. H., Rahman, M. L., Rahim, M. H. A., & Sarkar, S. M. (2016). Highly Active Kenaf Bio-Cellulose Based Poly(hydroxamic acid) Copper Catalyst for Aza-Michael Addition and Click Reactions. *ChemistrySelect*, *1*(11), 2750–2756.

Marion, N., Ecarnot, E. C., Navarro, O., Amoroso, D., Bell, A., & Nolan, S. P. (2006). (IPr)Pd(acac)Cl : An Easily Synthesized, Efficient, and Versatile Precatalyst for C-N and C-C Bond Formation. *Journal of Organic Chemistry*, *71*, 3816-3821.

Marion, N., Navarro, O., Mei, J., Stevens, E. D., Scott, N. M., & Nolan, S. P. (2006). Modified (NHC)Pd(allyl)Cl (NHC=*N*-Heterocyclic Carbene) Complexes for Room-Temperature Suzuki - Miyaura and Buchwald - Hartwig Reactions. *Journal of the American Chemical Society*, *128*(11), 4101-4111.

Marques, C. A., & Machado, A. A. S. C. (2014). Environmental Sustainability: Implications and limitations to Green Chemistry. *Foundations of Chemistry*, *16*(2), 125–147.

Marulasiddeshwara, M. B., & Kumar, P. R. (2016). Synthesis of Pd(0) nanocatalyst using lignin in water for the Mizoroki–Heck reaction under solvent-free conditions. *International Journal of Biological Macromolecules*, *83*, 326–334.

McDowall, D. J., Gupta, B. S., & Stannett, V. T. (1984). Grafting of vinyl monomers to cellulose by ceric ion initiation. *Progress in Polymer Science*, *10*(1), 1–50.

McGlacken, G. P., & Bateman, L. M. (2009). Recent advances in aryl–aryl bond formation by direct arylation. *Chemical Society Reviews*, *38*(8), 2447-2464.

Mekhzoum, M. E. M., Benzeid, H., Qaiss, A. E. K., Essassi, E. M., & Bouhfid, R. (2016). Copper(I) Confined in Interlayer Space of Montmorillonite: A Highly Efficient and Recyclable Catalyst for Click Reaction. *Catalysis Letters*, *146*(1), 136–143.

Meldal, M. (2008). Polymer "Clicking" by CuAAC reactions. *Macromolecular Rapid Communications*, *29*(12-13), 1016–1051.

Mino, T., Suzuki, S., Hirai, K., Sakamoto, M., & Fujita, T. (2011). Hydrazone-promoted Sonogashira coupling reaction with aryl bromides at low palladium loadings. *Synlett*, (9), 1277–1280.

Miyaura, N., Yanagi, T., & Suzuki,A. (1981). The Palladium-Catalyzed Cross-Coupling reaction of Phenylboronic Acid with Haloarenes in the Presence of Bases. *Synthetic Communications*, *11*(7), 513-519.

Mirsafaei, R., Heravi, M. M., Ahmadi, S., Moslemin, M. H., & Hosseinnejad, T. (2015). In situ prepared copper nanoparticles on modified KIT-5 as an efficient recyclable catalyst and its applications in Click reactions in water. *Journal of Molecular Catalysis A: Chemical*, *402*, 100–108.

Mizoroki, T., Mori, K., & Ozaki, A. (1971). Arylation of Olefin with Aryl Iodide Catalyzed by Palladium. *Bulletin of the Chemical Society of Japan*, *44*, 581-581

Mohammadi, E., & Movassagh, B. (2016). Synthesis of polystyrene-supported Pd(II)-NHC complex derived from theophylline as an efficient and reusable heterogeneous catalyst for the Heck-Matsuda cross-coupling reaction. *Journal of Molecular Catalysis A: Chemical*, *418-419*, 158–167.

Molnár, Á. (2011). Efficient, selective, and recyclable palladium catalysts in carbon-carbon coupling reactions. *Chemical Reviews*, *111*(3), 2251–2320.

Mondal, M. I. H., Yeasmin, M. S., & Rahman, M. S. (2015). Preparation of food grade carboxymethyl cellulose from corn husk agrowaste. *International Journal of Biological Macromolecules*, *79*, 144–150.

Morán, J. I., Alvarez, V. A., Cyras, V. P., & Vázquez, A. (2008). Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose*, *15*(1), 149–159.

Mori, K., Mizoroki, T., & Ozaki, A. (1973). Arylation of Olefin with Iodobenzene Catalyzed by Palladium. *Bulletin of the Chemical Society of Japan*, *46*, 1505-1508.

Movassagh, B., Tahershamsi, L., & Mobaraki, A. (2015). A magnetic solid sulfonic acid modified with hydrophobic regulators: An efficient recyclable heterogeneous catalyst for one-pot Aza-Michael-type and Mannich-type reactions of aldehydes, ketones, and amines. *Tetrahedron Letters*, *56*(14), 1851–1854.

Naeimi, H., & Shaabani, R. (2017). Ultrasound promoted facile one pot synthesis of triazole derivatives catalyzed by functionalized graphene oxide Cu(I) complex under mild conditions. *Ultrasonics Sonochemistry*, *34*, 246–254.

Naghipour, A., & Fakhri, A. (2016). Heterogeneous Fe_3O_4@chitosan-Schiff base Pd nanocatalyst: Fabrication, characterization and application as highly efficient and magnetically-recoverable catalyst for Suzuki-Miyaura and Heck-Mizoroki C-C coupling reactions. *Catalysis Communications*, *73*, 39–45.

Negishi, E. I., King, A. O., & Okukado, N. (1977). Selective carbon-carbon bond formation via transition metal catalysis. 3. A highly selective synthesis of unsymmetrical biaryls and diarylmethanes by the nickel or palladium-catalyzed reaction of aryl and benzylzinc derivatives with aryl halides. *The Journal of Organic Chemistry*, *42*(10), 1821–1823.

Nguyen, L. T. L., Nguyen, T. T., Nguyen, K. D., & Phan, N. T. S. (2012). Metal-organic framework MOF-199 as an efficient heterogeneous catalyst for the Aza-Michael reaction. *Applied Catalysis A: General*, *425-426*, 44–52.

Nicolaou, K. C., Bulger, P. G., & Sarlah, D. (2005). Palladium-catalyzed cross-coupling reactions in total synthesis. *Angewandte Chemie International Edition*, *44*(29), 4442–4489.

Nieman, G. W., Weertman, J. R., & Siegel, R. W. (1991). Mechanical behavior of nanocrystalline Cu and Pd. *Journal of Materials Research*, *6*(05), 1012–1027.

Oger, N., Le Grognec, E., & Felpin, F. X. (2014). Continuous-flow Heck-Matsuda reaction: Homogeneous versus heterogeneous palladium catalysts. *Journal of Organic Chemistry*, *79*(17), 8255-8262.

Ozawa, F., Kubo, A., Matsumoto, Y., Hayashi, T., Nishioka, E., Yanagi, K., & Moriguchi, K. I. (1993). Palladium-Catalyzed Asymmetric Arylation of 2,3-Dihydrofuran with Phenyl Triflate. A Novel Asymmetric Catalysis Involving a Kinetic Resolution Process. *Organometallics*, *12*(10), 4188–4196.

Pagliaro, M., Pandarus, V., Béland, F., Ciriminna, R., Palmisano, G., & Carà, P. D. (2011). A new class of heterogeneous Pd catalysts for synthetic organic chemistry. *Catalysis Science & Technology*, *1*(5),736-739.

Paul, S., Islam, M. M., & Islam, S. M. (2015). Suzuki–Miyaura reaction by heterogeneously supported Pd in water: recent studies. *RSC Advances*, *5*(53), 42193–42221.

Peñafiel, I., Pastor, I. M., & Yus, M. (2012). Heck-Matsuda reactions catalyzed by a hydroxyalkyl-functionalized NHC and palladium acetate. *European Journal of Organic Chemistry*, (16), 3151–3156.

Petroni, A., Bertazzo, A., Sarti, S., & Galli, C. (1989). Accumulation of Arachidonic Acid Cyclo and Lipoxygenase Products in Rat Brain During Ischemia and Reperfusion: Effects of Treatment with GM1-Lactone. *Journal of Neurochemistry*, *53*(3), 747–752.

Phapale, V. B., & Cárdenas, D. J. (2009). Nickel-catalysed Negishi cross-coupling reactions: scope and mechanisms. *Chemical Society Reviews*, *38*(6), 1598–1607.

Pontes da Costa, A., Rosa Nunes, D., Tharaud, M., Oble, J., Poli, G., & Rieger, J. (2017). Pd(0)-Nanoparticles Embedded in Core-Shell Nanogels as Recoverable Catalysts for the Mizoroki-Heck Reaction. *ChemCatChem*, *9(12)*, 2167–2175.

Prenesti, E., & Berto, S. (2002). Interaction of copper(II) with imidazole pyridine nitrogen-containing ligands in aqueous medium: A spectroscopic study. *Journal of Inorganic Biochemistry*, *88*(1), 37–43.

Pryjomska-Ray, I., Gniewek, A., Trzeciak, A. M., Ziółkowski, J. J., & Tylus, W. (2006). Homogeneous/heterogeneous palladium based catalytic system for Heck reaction. The reversible transfer of palladium between solution and support. *Topics in Catalysis*, *40*(1-4), 173–184.

Quignard, F., Choplin, A., & Domard, A. (2000). Chitosan: A natural polymeric support of catalysts for the synthesis of fine chemicals. *Langmuir*, *16*(24), 9106–9108.

Rahman, L., Rohani, N., Mustapa, N., & Yusoff, M. M. (2014). Synthesis of Polyamidoxime Chelating Ligand from Polymer-Grafted Corn-Cob Cellulose for Metal Extraction, *Journal of Applied Polymer Science*, *40833*, 1–8.

Rahman, M. L., Sarkar, S. M., Yusoff, M. M., & Abdullah, M. H. (2016). Efficient removal of transition metal ions using poly(amidoxime) ligand from polymer grafted kenaf cellulose. *RSC Advances*, *6*(1), 745–757.

Rai, R. K., Tyagi, D., Gupta, K., & Singh, S. K. (2016). Activated nanostructured bimetallic catalysts for C–C coupling reactions: recent progress. *Catalysis Science and Technology*, *6*(10), 3341–3361.

Rangel Rangel, E., Maya, E. M., Sánchez, F., de la Campa, J. G., & Iglesias, M. (2015). Palladium-heterogenized porous polyimide materials as effective and recyclable catalysts for reactions in water. *Green Chemistry*, *17*(1), 466–473.

Reddy, K. R., & Kumar, N. S. (2006). Cellulose-supported copper(0) catalyst for Aza-Michael addition. *Synlett*, (14), 2246–2250.

Reddy, K. R., Kumar, N. S., Sreedhar, B., & Kantam, M. L. (2006). *N*-Arylation of nitrogen heterocycles with aryl halides and arylboronic acids catalyzed by cellulose supported copper(0). *Journal of Molecular Catalysis A: Chemical*, *252*(1-2), 136–141.

Rossy, C., Majimel, J., Tréguer, M., Fouquet, E., & Felpin, F. (2014). Palladium and copper-supported on charcoal : A heterogeneous multi-task catalyst for sequential Sonogashira-Click and Click-Heck reactions. *Journal of Organometallic Chemistry*, *755*, 78–85.

Roy, S., Chatterjee, T., Pramanik, M., Roy, A. S., Bhaumik, A., & Islam, S. M. (2014). Cu(II)-anchored functionalized mesoporous SBA-15: An efficient and recyclable catalyst for the one-pot Click reaction in water. *Journal of Molecular Catalysis A: Chemical*, *386*, 78–85.

Sanchez-Rosello, M., Acena, J. L., Simon-Fuentes, A., & del Pozo, C. (2014). A general overview of the organocatalytic intramolecular Aza-Michael reaction. *Chemical Society Reviews*, *43*(21), 7430–7453.

Sarkar, S. M., Rahman, M. L., Chong, K. F., & Yusoff, M. M. (2017). Poly(hydroxamic acid) palladium catalyst for heck reactions and its application in the synthesis of Ozagrel. *Journal of Catalysis*, *350*, 103–110.

Sarkar, S. M., Rahman, M. L., & Yusoff, M. M. (2015). Pyridinyl functionalized MCM-48 supported highly active heterogeneous palladium catalyst for cross-coupling reactions. *RSC Advances*, *5*(25), 19630–19637.

Sarkar, S. M., Sultana, T., Biswas, T. K., Rahman, M. L., & Yusoff, M. M. (2016). Waste corn-cob cellulose supported bio-heterogeneous copper nanoparticles for Aza-Michael reactions. *New Journal of Chemistry*, *40*(1), 497–502.

Schatz, A., Reiser, O., & Stark, W. J. (2010). Nanoparticles as semi-heterogeneous catalyst supports. *Chemistry-A European Journal*, *16*(30), 8950–8967.

Schmidt, B., & Wolf, F. (2017). Synthesis of Phenylpropanoids via Matsuda−Heck Coupling of Arene Diazonium Salts. *Journal of Organic Chemistry*, *82*, 4386-4395.

Selvakumar, K., Zapf, A., Spannenberg, A., & Beller, M. (2002). Synthesis of monocarbenepalladium(0) complexes and their catalytic behavior in cross-coupling reactions of aryldiazonium salts. *Chemistry-A European Journal*, *8*(17), 3901–3906.

Shang, N., Gao, S., Zhou, X., Feng, C., Wang, Z., & Wang, C. (2014). Palladium nanoparticles encapsulated inside the pores of a metal–organic framework as a highly active catalyst for carbon–carbon cross-coupling. *RSC Advances*, *4*(97), 54487–54493.

Sharpless, K. B., & Manetsch, R. (2006). Click Chemistry: A Powerful Means for Lead Discovery. *Expert Opinion on Drug Discovery*, *1*(6), 525–538.

Sheldon, R. A. (2012). Fundamentals of green chemistry: efficiency in reaction design. *Chemical Society Reviews*, *41*(4), 1437–1451.

Sheldon, R. A. (2014). Green and sustainable manufacture of chemicals from biomass: state of the art. *Green Chemistry*, *16*(3), 950–963.

Shen, C., Shen, H., Yang, M., Xia, C., & Zhang, P. (2015). A novel D-glucosamine-derived pyridyl-triazole@palladium catalyst for solvent-free Mizoroki–Heck reactions and its application in the synthesis of Axitinib. *Green Chemistry*, *17*, 225–230.

Shi, W., Liu, C., & Lei, A. (2011). Transition-metal catalyzed oxidative cross-coupling reactions to form C–C bonds involving organometallic reagents as nucleophiles. *Chemical Society Reviews*, *40*(5), 2761-2776.

Shibasaki, M., & Vogl, E. M . (1999). The palladium-catalysed arylation and vinylation of alkenes-enantioselective fashion. *Journal of Organometallic Chemistry*, *576*, 1–15.

Shirakawa, E., Yoshida, H., Nakao, Y., & Hiyama, T. (1999). Palladium-catalyzed dimerization-carbostannylation of alkynes: Synthesis of highly conjugated alkenylstannanes. *Journal of the American Chemical Society*, *121*(17), 4290–4291.

Siew, S., Wen, Y., Rahman, L., Arshad, S. E., Surugau, N. L., & Musta, B. (2011). Synthesis and characterization of poly(hydroxamic acid)–poly(amidoxime) chelating ligands from polymer-grafted acacia cellulose. *Journal of Applied Polymer Science, 124(6)*, 4443-4451.

Smith, A. K., & Basset, J. M. (1977). Transition metal cluster complexes as catalysts. A review. *Journal of Molecular Catalysis*, *2*(4), 229–241.

Sobhani, S., & Pakdin-Parizi, Z. (2014). Palladium-DABCO complex supported on γ-Fe_2O_3 magnetic nanoparticles: A new catalyst for C-C bond formation via Mizoroki-Heck cross-coupling reaction. *Applied Catalysis A: General*, *479*, 112–120.

Sodhi, R. K., Paul, S., Gupta, V. K., & Kant, R. (2015). Conversion of *α, β*-unsaturated ketones to 1,5-diones via tandem retro-Aldol and Michael addition using $Co(acac)_2$ covalently anchored onto amine functionalized silica. *Tetrahedron Letters*, *56*(15), 1944–1948.

Sonogashira, K., Tohda, Y., & Hagihara, N. (1975). A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes and bromopyridines. *Tetrahedron Letters*, *16*(50), 4467–4470.

Srivastava, N., & Banik, B. K. (2003). Bismuth nitrate-catalyzed versatile Michael reactions. *Journal of Organic Chemistry*, *68*(6), 2109–2114.

Su, D. S., Zhang, J., Frank, B., Thomas, A., Wang, X., Paraknowitsch, J., & Schlögl, R. (2010). Metal-free heterogeneous catalysis for sustainable chemistry. *Chem. Sustainble Chemistry*, *3*(2), 169–180.

Sukhov, D. (2016). Quick non-destructive analysis of lignin condensation and precipitation by FTIR. *Cellulose Chemistry and Technology 50*(2), 213–217.

Sultana, T., Mandal, B. H., Rahman, M. L., & Sarkar, S. M. (2016). Bio-Waste Corn-cob Cellulose Supported Poly(amidoxime) Palladium Nanoparticles for Suzuki-Miyaura Cross-Coupling Reactions. *ChemistrySelect*, *1*(13), 4108–4112.

Sunaba, H., Kamata, K., & Mizuno, N. (2014). Selective N-alkylation of indoles with *α,β*-unsaturated compounds catalyzed by a monomeric phosphate. *ChemCatChem*, *6*(8), 2333–2338.

Suzuki, A. (1999). Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. *Journal of Organometallic Chemistry*, *576*(1-2), 147–168.

Swadźba-Kwaśny, M., Chancelier, L., Ng, S., Manyar, H. G., Hardacre, C., & Nockemann, P. (2012). Facile in situ synthesis of nanofluids based on ionic liquids and copper oxide clusters and nanoparticles. *Dalton Transactions*, *41*(1), 219–227.

Tasker, S. Z., Gutierrez, A. C., & Jamison, T. F. (2014). Nickel-catalyzed Mizoroki-Heck reaction of aryl sulfonates and chlorides with electronically unbiased terminal olefins: High selectivity for branched products. *Angewandte Chemie - International Edition*, *53*(7), 1858–1861.

Tavassoli, M., Landarani-Isfahani, A., Moghadam, M., Tangestaninejad, S., Mirkhani, V., & Mohammadpoor-Baltork, I. (2015). Polystyrene-supported ionic liquid copper complex: A reusable catalyst for one-pot three-component Click reaction. *Applied Catalysis A: General*, *503*, 186–195.

Taylor, P., Turker, M. F., Ayaz, H., & Kaygusuz, K. (2010). Forest Biomass as a Source of Renewable Energy in Turkey. *North*, *8312*, 37–41.

Torborg, C., & Beller, M. (2009). Recent applications of palladium-catalyzed coupling reactions in the pharmaceutical, agrochemical, and fine chemical industries. *Advanced Synthesis and Catalysis*, *351*(18), 3027–3043.

Tsuji, Y., & Fujihara, T. (2007). Homogeneous nanosize palladium catalysts. *Inorganic Chemistry*, *46*(6), 1895–1902.

Urgaonkar, S., Xu, J. H., & Verkade, J. G. (2003). Application of a New Bicyclic Triaminophosphine Ligand in Pd-Catalyzed Buchwald-Hartwig Amination Reactions of Aryl Chlorides, Bromides, and Iodides. *Journal of Organic Chemistry*, *68*(22), 8416–8423.

Vadaparthi, P. R. R., Pavan Kumar, C., Kumar, K., Venkanna, A., Lakshma Nayak, V., Ramakrishna, S., & Babu, K. S. (2015). Synthesis of costunolide derivatives by Pd-catalyzed Heck arylation and evaluation of their cytotoxic activities. *Medicinal Chemistry Research*, *24*(7), 2871–2878.

Wan, Z., Xiong, Z., Ren, H., Huang, Y., & Liu, H. (2011). Graft copolymerization of methyl methacrylate onto bamboo cellulose under microwave irradiation. *Carbohydrate Polymers*, *83*(1), 264–269.

Wang, Y., Yuan, Y. Q., & Guo, S. R. (2009). Silica sulfuric acid promotes Aza-Michael addition reactions under solvent-free condition as a heterogeneous and reusable catalyst.*Molecules*, *14*(11), 4779–4789.

Wei, W., Zhu, H., Zhao, C., Huang, M., & Jiang, Y. (2004). Asymmetric hydrogenation of furfuryl alcohol catalyzed by a biopolymer–metal complex, silica-supported alginic acid–amino acid–Pt complex. *Reactive & Functional Polymers*, *59*, 33–39.

Wenda, S., Illner, S., Mell, A., & Kragl, U. (2011). Industrial biotechnology-the future of green chemistry. *Green Chemistry*, *13*(11), 3007-3047.

Wesselbaum, S., Vom Stein, T., Klankermayer, J., & Leitner, W. (2012). Hydrogenation of carbon dioxide to methanol by using a homogeneous ruthenium-phosphine catalyst. *Angewandte Chemie International Edition*, *51*(30), 7499–7502.

William, D., Connell, O., Birkinshaw, C., Francis, T., & Dwyer, O. (2008). Heavy metal adsorbents prepared from the modification of cellulose : A review. *Bioresource Technology*, *99*, 6709-6724.

Wu, H., Li, H., Kwok, R. T. K., Zhao, E., Sun, J. Z., Qin, A., & Tang, B. Z. (2014). A recyclable and reusable supported Cu(I) catalyzed azide-alkyne Click polymerization. *Scientific Reports*, *4*, 1-5.

Wu, S., Ma, H., Jia, X., Zhong, Y., & Lei, Z. (2011). Biopolymer-metal complex wool-Pd as a highly active heterogeneous catalyst for Heck reaction in aqueous media. *Tetrahedron*, *67*(1), 250–256.

Xie, S. L., Hui, Y. H., Long, X. J., Wang, C. C., & Xie, Z. F. (2013). Aza-Michael addition reactions between nitroolefins and benzotriazole catalyzed by MCM-41 immobilized heteropoly acids in water. *Chinese Chemical Letters, 24*(1), 28–30.

Xu, G., Zhang, Y., Wang, K., Fu, Y., & Du, Z. (2015). Microwave-assisted Stille cross-coupling reaction catalysed by in situ formed palladium nanoparticles. *Journal of Chemical Research, 39*(7), 399–402.

Xu, J. M., Wu, Q., Zhang, Q. Y., Zhang, F., & Lin, X. F. (2007). A basic ionic liquid as catalyst and reaction medium: A rapid and simple procedure for Aza-Michael addition reactions. *European Journal of Organic Chemistry*, (11), 1798–1802.

Yamada, Y. M. A, Sarkar, S. M., & Uozumi, Y. (2012). Amphiphilic self-assembled polymeric copper catalyst to parts per million levels: Click chemistry. *Journal of the American Chemical Society, 134*(22), 9285–9290.

Yamada, Y. M. A, Yuyama, Y., Sato, T., Fujikawa, S., & Uozumi, Y. (2014). A palladium-nanoparticle and silicon-nanowire-array hybrid: A platform for catalytic heterogeneous reactions. *Angewandte Chemie International Edition, 53*(1), 127–131.

Yang, J., Tan, X., Wang, Y., & Wang, X. (2013). Ethylenediamine-functionalized activated carbon anchored palladium complex: A recyclable catalyst for Heck reaction. *Journal of Porous Materials, 20*(3), 501–506.

Yang, L., Xu, L. W., & Xia, C. G. (2007). Efficient catalytic Aza-Michael additions of carbamates to enones: revisited dual activation of hard nucleophiles and soft electrophiles by $InCl_3$/TMSCl catalyst system. *Tetrahedron Letters, 48*(9), 1599–1603.

Ying, A., Zhang, Q., Li, H., Shen, G., Gong, W., & He, M. (2013). An environmentally benign protocol: Catalyst-free Michael addition of aromatic amines to α,β-unsaturated ketones in glycerol. *Research on Chemical Intermediates, 39*(2), 517–525.

Yoshida, K., Gonzalez-Arellano, C., Luque, R., & Gai, P. L. (2010). Efficient hydrogenation of carbonyl compounds using low-loaded supported copper nanoparticles under microwave irradiation. *Applied Catalysis A: General, 379*(1-2), 38–44.

Yu, W., Jiang, L., Shen, C., Xu, W., & Zhang, P. (2016). A highly efficient synthesis of *N*-glycosyl-1,2,3-triazoles using a recyclable cellulose-copper(0) catalyst in water. *Catalysis Communications, 79*, 11–16.

Zhang, X., Geng, Y., Han, B., Ying, M., Huang, M., & Jiang, Y. (2001). Asymmetric Hydrogenation of Ketones Catalyzed by Zeolite-supported Gelatin-Fe Complex. *Polymers for Advanced Technologies, 12*, 642–646.

Zhou, X., Xu, W., Liu, G., Panda, D., & Chen, P. (2010). Size Dependent Catalytic Activity and Dynamics of Gold Nanoparticles at the Single-Molecule Level. *Journal of the American Chemical Society*, *132*(11), 138–146.